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Antifungal activities of Ruthenium (III) complexes derived from chitosan based schiff base

Chemistry

KEYWORDS : Chitosan schiff base, Ruthenium (III) complex, FT-IR, TGA, Antifungal study.

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ABSTRACT

Chitosan based schiff base and their Ruthenium (III) complexes [Ru ($C_{24}H_{53}N_2O_{10}$) Cl].H_2O and [Ru ($C_{23}H_{50}N_2O_9$) Cl].H_2O were synthesized and characterized by Elemental analysis, FT-IR, and Thermo-gravimetric analysis (TGA). Antifungal activities of the complexes were analyzed against Aspergillus flavus, Aspergillus niger, Penicillium chrysogenum, Trichoderma viride and Fusarium oxysporum in disc diffusion method. The results showed better inhibitory properties against the fungal organisms.

1. Introduction

is the principal derivative of chitin produced by alkaline deacetylation of chitin, which consists of poly β-(1-4)-2-acetamido-2-deoxy-β-D-glucopyranose units. Also, it is most important and abundant polysaccharide being second only to cellulose isolated from different natural sources such as crustacean, molluscs and insects. The major constituent of the exosketon of insects and in certain fungi, where it is the principal fibbriller biopolymer in the cell wall1-5. The polymeric property of chitosan possess an important physiological properties such as biocompatible, biodegradable, and non-allergenic and this shows various functional properties, which has been applied in many fields such as chromatographic separations, photography, food processing, cosmetics, biomedicine, agriculture, environmental protection, wastewater management, fibre industries and solid state batteries6-8.

This work explicit to characterize the ruthenium (III) complexes derived from schiff base ligands through the synthesis, characterization, and antifungal activities of ruthenium(III)complexes.

Experimental

2.1 Materials

Chitosan was purchased from Sigma-Aldrich Chemical Co., Bangalore, India with a deacetylation percentage in the range of 85 – 90%. All aldehydes were obtained from Merck, Mumbai, India. Acetic acid and ethanol (AR) were obtained from SD fine chemicals, Mumbai. Ruthenium (III) Chloride (98% Purity) was obtained from Avra Synthesis, Hyderabad, India.

2.2 Instrumentation

The FTIR spectra were measured with FT-IR Shimadzu, Prestige-21 Spectrophotometer. Thermal analysis measurement were made in the 40° C – 600° C range at a heating rate 10° C minimum, using Alumel, Perk alloy, and Iron as the references, on a Pyris-6 analyzer TGA – 4000.

2.3 Preparation of Chitosan – Schiff base ligands and their metal complexes

2.3.1 Preparation of Chitosan – 4-hydroxy-3-methoxy benzaldehyde schiff base ligand.

It was prepared by the condensation of a suspension of 1 g of chitosan with small amount of acetic acid and 0.82 g of 4-hydroxy-3-methoxy benzaldehyde in 20 ml of ethanol. This mixture was stirred at room temperature for 1 h followed by heating for 12 h under water bath at 60° C. The yellow colour product was filtered off, washed with ethanol and dried in vacuo. FT-IR: γ (CH N), 1649; (CH), 1288; Analytical calculation: $C_{24}H_{53}N_2O_{10}$: C 54.42, H 10.09, N 5.29, O 30.21

2.3.2 Preparation of Chitosan – 2-hydroxy benzaldehyde schiff base ligand.

About 1 g of chitosan powder was dissolved in 25 ml of ethanol with a small amount of acetic acid, shake well until chitosan emulsion was obtained. By adding slowly to the solution of 0.87 g of 2-hydroxy benzaldehyde was also dissolved in 25 ml ethanol. The solution mixture was stirred, and heated for 12 h under water bath at 60° C. The bright yellow colour product was filtered, washed with ethanol and dried *in vacuo.* FT-IR: γ (CH N), 1629; (CH), 1278; Analytical calculation: $C_{23}H_{50}N_2O_9$: C 55.40, H 10.11, N 5.62, O 28.88.

2.3.3 Preparation of Schiff base Ruthenium(III)complexes: [Ru($C_{24}H_{53}N_2O_{10}$) Cl].H_2O and [Ru ($C_{23}H_{50}N_2O_9$) Cl].H_2O.

To a suspension of chitosan ligands (0.2 g) in 10 ml of ethanol and a solution of $RuCl_3$ (0.15 g) in ethanol was added slowly to it. The mixture was stirred and heated for 12 h under water bath at 60° C. The brown colour product was filtered off, washed with excess of ethanol and dried in vacuo. FT-IR: γ (CH N), 1608; (CH), 1200; (Ru-O), 500-600; (Ru-N), 400-500; (Ru-Cl), 300-400; Analytical calculation for [Ru ($C_{24}H_{53}N_2O_{10}$) Cl].H_2O: C 42.13, H 8.10, Cl 5.18, N 4.09, O 25.7 Ru 14.77 and [Ru ($C_{23}H_{50}N_2O_9$) Cl].H_2O. : C 42.36, H 7.88, Cl 5.44, N 4.30, O 24.53, Ru 15.50.

3. Results and discussion

3.1 Infra Spectroscopy

FT-IR spectra of chitosan, exhibits strong peak at 3379 cm-1 which can be assigned due to coaxial stretching vibration of O-H superimposed to the N-H stretching band and inter hydrogen bands of the polysaccharide. The C-H axial stretching band arises at 2881 cm-1. The other important observed characteristic bands of chitosan are bands due to the primary amine 2358 cm-1, band due to the $-NHCOH_3$ (acetyl) units (with C=O stretching) at 1851cm-1, with (N-H bending) at 1554 cm-1, and with C-H stretching coupled with N-H plan deformation at 1421 cm-1, besides the two characteristic polysaccharide bands are 1151 cm-1 and 1072 cm-1due to C-O stretching from β-(1-4) glycosidic unit**9**.

In the FT-IT spectrum the Schiff base ligands show a strong band at 1649 cm-1 and 1629 cm-1 which are characteristic stretching frequency of azomethine group (C N). On complexation these bands are shifted to 1608 cm-1 and 1610 cm-1 ranges respectively. This indicates that the imino nitrogen in all ligands is coordinated to the metal ion10, 11.

In FT-IR spectrum show that the phenolic stretching are shifted to higher frequency band at 1068 cm-1 and 1076 cm-1 due to the coordination of the phenolic group with the metal. Further, the –OH absorption bands are observed between at 2885 cm-1 and 2983 cm-1 in free Schiff base but it was disappeared in their complexes, indicating that deprotonation of both phenolic (2-OH) proton prior to coordination12-14. And two bands arrived at 1070 cm-1 in the IR spectrum of both Schiff bases respectively, which are characterized due to C-O-C symmetric stretching of methoxy ($R-O-CH_3$). And also important band arrived at 451 cm-1 indicating that the coordination bond is formed between metal ion and oxygen atom of methoxy. Moreover many bands are obtained between 600-400 cm-1, these bands may be assigned to the M-O, M-N and M-Cl stretching 15, 16.

3.2 Thermal Analysis

Thermo-gravimetric analysis curves of Ruthenium (III) complexes $[Ru(C_{24}H_{53}N_2O_{10})Cl].H_2O$ and $[Ru(C_{23}H_{50}N_2O_9)Cl].H_2O$ undergo a three-step weight loss under nitrogen atmosphere. The first stage decomposition occurred in the ranges from 90°C - 100°C with weight losses 10 % - 13 % respectively, ascribed to the loss of absorbed water. The thermal degradation of chitosan ligands occurs in the temperature ranges from 110°C – 225°C with weight losses from 22% - 30% respectively, due to the decomposition of saccharide ring of the polymer. In the second stage, the Schiff base undergoes the decomposition in the ranges from 250°C – 300°C with weight losses from 48 % - 56 % respectively. The ruthenium (III) complexes stable up to 300°C. At this stage decomposition occurs, and finally it gives RuO_2 in the temperature ranges from 300°C - 600°C with weight losses from 80 % - 90 % respectively.

3.3 Antifungal Activities

The results of antifungal studies show that the ruthenium chelates are more toxic compared with their parent ligands against the same micro-organisms and under the identical experimental conditions. The increase in antifungal activity of the metal chelates may be due to the effect of the metal ion on the normal cell process. A possible mode of toxicity increase may be considered in the light of Tweedy's chelation theory such chelation could enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layers of the cell membrane. $[Ru(C_{23}H_{50}N_2O_9)Cl].H_2O$ shows higher capacity than $[Ru(C_{24}H_{53}N_2O_{10})Cl].H_2O$. Normally, the inhibition activity increases with increase in the concentration of the solution. In this attempt the standard drug ciprofloxacin observed and ascertained in this investigation as mentioned above in all the efforts dimethyl sulfoxide is used as control. The antifungal results are furnished in table-1.

Table-1
Antifungal activity [disc diffusion method]

S. No.	Bacteria	Standard Antibiotic Disk*	Zone of inhibition (mm)		
			[Ru (C24H53N2O10) Cl].H2O	[Ru (C23H50N2O9) Cl].H2O	Control (DMSO)
1	Aspergillus flavus	30	11	11	-
2	Aspergillus niger	28	-	12	-
3	Penicillium chrysogenum	32	10	17	-
4	Trichoderma viride	32	11	12	-
5	Fusarium oxysporum	28	13	16	-

***ciprofloxacin.**

Conclusion

The new series of chitosan schiff base ruthenium (III) complexes were synthesized by the chemical reaction of chitosan with different aldehydes. The antifungal activities of the complexes and the ligands have been carried out against the fungi such as Aspergillus flavus, Aspergillus niger, Penicillium chrysogenum, Trichoderma viride, Fusarium oxysporum using nutrient agar medium by disc diffusion method with an incubation period of 18 h at 37°C. The test solutions were prepared in DMSO which is used as a control. Generally, the ruthenium (III) complexes have shown higher antifungal activity than the other corresponding free ligands against the same micro organism under the same experimental conditions.

The results further support the fact that the ruthenium (III) complexes with potential substituent can enhance the antifungal activity increases with minimum concentration (1000 μg/ml). It was concluding that the antifungal activities of ruthenium (III) complexes have been increased on the basis of chelation theory.

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